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TECHNICAL REPORT

2015 Chemical-Agent Simulants Workshop Report

August 2016

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14. ABSTRACT

Very limited data exists in the conditions of interest (high temperatures, high heating rates) for simulating weapon defeat of targets containing chemical agent. The Defense Threat Reduction Agency (DTRA) is attempting to address this gap by funding basic research in this area. The purpose of the workshop was to identify and decide on a set of chemical simulants that would be most suitable for studying the reactivity and kinetics of chemical warfare agents (CWAs) under extreme temperature and heating rate conditions within a post-blast fireball. The expectations were to identify three to five simulants per chemical agent of interest, so as to focus basic research investigations.

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Executive Summary

A Chemical-Agent Simulants Workshop was held on 17 December 2015 at Lorton, Virginia hosted by the Defense Threat Reduction Agency (DTRA), Basic and Applied Sciences Department (J9-BA), Thrust Area 4 (TA4) "Science to Defeat WMD" program manager. The objective of the workshop was to decide on a set of chemical-agent simulants that is best for studying the reactivity and kinetics of chemical agents (CA) under extreme temperature and heating rate conditions within a post-blast fireball. These simulants could then be used in basic research projects on the topic "Chemistry of Chemical Agents, Simulants, and Precursors" being executed starting FY16, under Amendment 4 (December 2014) of the HDTRA1-11-16-BRCWMD-BAA Broad Agency Announcement.

The one-day workshop was physically attended by nearly 40 scientists or engineers, with about 10 more virtual attendees that called in and viewed presentations online using the workshop-provided web support. The US attendees were from universities, industry laboratories, and many DTRA Divisions. In addition, the United Kingdom's Defence Science and Technology Laboratory (DSTL) was represented by a few of their contractors.

The agenda included a summary of public-access publications and literature on chemical-agent simulants used in the past, any subsequent studies of reactions and kinetics of those simulants, and the physical properties of these well-used simulants. Other presentations included some recent combustion testing and modeling of one popular simulant (TEP), the UK's efforts on selecting simulants for their studies, and some of the basic research proposed to be funded by DTRA. The presentations were followed by 2-hours of discussion on various simulants whose activation barrier to high-temperature reaction, evaporation rate, availability, safety/handling, etc. may make them suitable for use in these basic research projects. The entire Agenda can be found in Appendix A.

The outcome from the workshop was to identify a moderate group of simulants in the hope that each of the basic research projects would study two to three of these simulants using their unique diagnostic techniques and capabilities, to span all of the simulants of interest across the range of temperatures and heating rates of interest. In this manner, a broad range of data would be collected, maximizing the utility of the research projects. Appendix B summarizes the selected simulants.

1. Introduction

A Chemical-Agent Simulants Workshop was hosted by the Defense Threat Reduction Agency (DTRA), Basic and Applied Sciences Department (J9-BA), Thrust Area 4 (TA4) "Science to Defeat WMD" program manager.

The mission of DTRA is to safeguard America and its allies from Weapons of Mass Destruction (WMD) by providing capabilities to reduce, eliminate, and counter the threat, and mitigate its effects. As such, DTRA supports research on ways and means to counter WMD, from basic studies to more applied technology. Often, Counter-WMD operations in non-permissive or access-denied environments rely on conventional weapons with energetic material payloads to defeat WMD targets. Current conventional weapons contain explosives and future custom-designed counter-WMD weapons will include reactive materials that continue to burn over longer periods of time than a conventional explosive. It is important to understand the effect of burning, variable heating rates, high temperature (high-T) and temperature duration, on chemical agents that could be contained in a WMD target. Particularly, asymmetric heating arising in multi-room structures where thermal delay/shielding and turbulence effects significantly vary temperatures and heating profiles over time.

Some important questions to be answered are: What intermediate reactive species and final products are formed as chemical agents/simulants/precursors are subjected to variable high temperatures and heating rates? What are the thermal degradation conditions and reaction rates? In addition, we must consider if any intermediate products of the high-T reactions, the final thermal-decomposition products, final combustion-reaction products, etc., could also be harmful or toxic, because that could exacerbate the WMD problem even as we perform counter-WMD operations! Further, since future weapons may contain reactive metals that burn to form metal oxides, or sulfates that form sulfides, or halogenated oxides that form halogens, any enhanced effect from metal oxides, sulfides or halogens are also of interest.

These high-T reactions and effects need to be characterized and understood to evaluate the full effect of counter-WMD operations on targets containing chemical agents, simulants and precursors. Therefore, DTRA published a topic titled "Chemistry of Chemical Agents, Simulants, and Precursors" in Amendment 4 (December 2014) of the HDTRA1-11-16-BRCWMD-BAA Broad Agency Announcement. At the time of the workshop the proposals submitted to this BAA topic were awaiting FY16 funding, and from the proposals and other discussions, it was clear that DTRA would need to provide some guidance to the university researchers on what agents or simulants to study.

Hence, the purpose of the Chemical-Agent Simulants Workshop was to identify a set of simulants that would be most ideal for studying the reactivity and kinetics of chemical warfare agents (CWAs) under extreme temperature and heating rate conditions within a post-blast fireball. The expectations were to identify the simulants of interest so as to focus efforts on three to five simulants for future basic

research investments. The workshop was set up to engage members of the agent-defeat community at DTRA, other US government agencies, industry, academia, and the United Kingdom's Defence Science and Technology Laboratory (DSTL) in interactive dialogue, including workshop-provided web support.

2. Presentations

To meet the objectives of the workshop, the agenda included presentations to review the current CWAs of interest, their known simulants and why those simulants were chosen. Additional presentations included the physical properties of chemical simulants and a review of research done by the U.S. Army Edgewood Chemical Biological Center (ECBC), who has worked with CWAs for several decades. Modelers' perspectives on data needed for modeling and simulation (M&S) of counter-WMD weapon effects were presented by both US and UK researchers. Since DSTL had recent experience with sorting through CWA simulants for their high-temperature testing in UK, their presentation on the criteria they used to select simulants was particularly helpful. The final set of presentations was given by some of the university principal investigators to potentially be funded under the BAA. The presentation by Southwest Research Institute (SwRI) based in San Antonio, TX was unique because of their prior experience and previous studies on High-T reactions of actual CWAs and some simulants. The workshop agenda is included in Appendix A.

2.1 Literature Review of Agents and Simulants, Dr. Yasmine Aly, J9BA, DTRA

The presentation included a list of known agent 'classes' and their simulants as detailed in Bartelt-Hunt et al. (2008) "A Review of Chemical Warfare Simulants for the Study of Environmental Behavior", *Critical Reviews in Environmental Science and Technology*, 38:2, pp. 112-136. This list included:

- Mustard (HD) and simulants - CEES (Half-Mustard), CEPS, Diethyl malonate, CEMS, Diethyl adipate, Methyl salicylate, Diethyl pimelate, and Dimethyl adipate
- Sarin (GB) and simulants – BUSH, TMP, DEEP, Paraoxon, DMMP, DPCP, DFP, TEP, DEM, DIMP
- Nerve Agent VX and simulants – DEP, DES, BIS, Malathion, DEM, Parathion, DEPPT, Amiton

The presentation also included reactions and mechanisms of agents and simulants as detailed in Glaude et al. (2002) "Detailed Chemical Kinetic Reaction Mechanisms for Incineration of Organophosporus and Fluoro-phosphorus Compounds" by LLNL, submitted to the 29th International Symposium on Combustion, in Japan, and further detailed reaction mechanisms of DEMP, DIMP and TEP as published in Glaude et al. (2000) "Kinetic Study of the Combustion of Organophosphorus Compounds," *Proceedings of the Combustion Institute*, 28, pp. 1749-1756.

Since Tri-Ethyl Phosphate (TEP) has been popularly used as a simulant in many large-scale tests, the chemical reaction mechanism of TEP as published in Zegers and Fisher (1998) "Pyrolysis of Triethyl Phosphate," *Combustion Science and Technology*, 138, pp. 85-103, was discussed in detail.

It was pointed out that most literature studies focus on pyrolysis (thermal decomposition) whereas

the new basic research efforts would focus on high-T reactions in air (combustion).

2.2 Physical Properties of CWAs and Their Simulants, Dr. David Tevault, US Army ECBC

The talk included a list of physical properties under investigation at ECBC including vapor pressure, melting point, density, viscosity, surface tension, solubility, and flash point, and some of these properties are listed in Appendix C. Measurement capabilities available at ECBC and the approaches/methodologies/instruments used in measuring different physical properties were presented, e.g., differential scanning calorimetry and gas saturation for vapor pressure determination, an oscillating U-tube for density measurements, capillary viscometry for viscosity, Wilhelmy plate for surface tension, etc. The presentation also featured a list of recently published, public-release reports by ECBC, shown below:

1. Thermophysical Properties of VX and RVX, *J. Chem. Eng. Data*, 2012, 57, 1970
2. Vapor Pressure of 1-Octanol below 5 kPa using DSC, *Thermochimica Acta*, 561, 2013, 72
3. Vapor Pressure of 2-Dialkyl Aminoethanethiols, *JCED*, 2013, 58, 1679
4. Vapor Pressure Data Analysis and Correlation Methodology for Data Spanning the Melting Point, ECBC-CR-135, 2013
5. *Vapor Pressure of Thiodiglycol, JCED,* 2014, 59, 307
6. Vapor Pressure of Triethyl and Tri-n-Propyl Phosphates and Diethyl Malonate, *JCED*, 2014, 59, 2649
7. Vapor Pressure of Methyl Salicylate and Hexadecane, ECBC-TR-1184, 2014
8. Thermophysical Properties and Spectral Characterization of EA 6043, ECBC-TR-1269, 2014
9. Vapor Pressure Determination of VM Using the Denuder-LC/MS Technique, ECBC-TR-1278, 2015
10. Vapor Pressure of DICDI, ECBC-TR-1352, 2016
11. Selected Thermophysical Properties of GP and 2,2-Dimethylcyclopentanol, *JCED*, in press
12. Critical Review of GA Vapor Pressure Data, ECBC-TR, in press

2.3 Chemical Kinetics of Agent Simulants: A High-Fidelity Modeler's Perspective, Dr. Andrea Zambon, CRAFT Tech.

This presentation gave an overview of the agent defeat problem and provided insights to the role of high-fidelity modeling and its capabilities. Zambon posed a key question: Does released mass contain active/viable agent or harmful byproducts? Not a simple undertaking! First the "source term" must be effectively represented in the model with understanding of early-time physics. Then finite-rate chemistry effects of agent neutralization together with turbulent mixing effects must be considered. The effects of finite-rate chemistry (ignition and extinction of an event) may play an important role when modeling the scales of motion in the post-detonation environment. Problems exist with this though, including the disparity in the chemical time scales and the complex kinetics of large fuel molecules. Hence the need for accurate chemical reaction mechanisms. In addition to finite-rate chemistry, intense small-scale turbulent mixing on rate processes may be very significant as well. This involves turbulent chemistry interaction (flame portion) and the heterogeneous combustion. It is impossible to employ a sufficient grid in the model to accurately resolve chemistry

(that occurs at molecular scales) and small-scale turbulent mixing. A solution to this problem is to sub-grid the turbulent combustion models.

Zambon then posed the computational challenges of chemical kinetics modeling. These include: the number of species (transport), number of reactions (Arrhenius rate exponentiation), Jacobian issues (evaluation and decomposition), stiffness (restrictive integration time step due to disparity on characteristic chemical time scales). For CFD simulations of realistic AD scenarios, 20-30 chemical species at most, are desirable. A proposed approach for chemical kinetics reduction is to survey available data as a starting point for predictions. The next step would be to develop a skeletal model and eliminate negligible/inactive species and reactions. Then one would develop a reduced model based on quasi steady-state approximations with automated reduction tools available (as explained in Zambon and Chelliah (2007), "Explicit Reduced Reaction Models for Ignition, Flame Propagation, and Extinction of $C_2H_4/CH_4/H_2$ and Air Systems", *Combustion and Flame*, 150:1, pp. 71-91). Finally, there needs to be extensive validation of every detailed, skeletal and reduced model for ignition/extinction predictions and validation of reduced models in CFD simulations.

A most important point made in this presentation was that the lack of detailed reaction mechanism information (constructed from rate measurements and first principles and validated) for both pyrolysis and oxidation studies was not available, especially at the correct thermochemical conditions relevant to AD problems.

2.4 Selection of Chemical Agent Simulants, Dr. Nick Robinson and Dr. Aaron Longbottom, DSTL, UK

This presentation made note that for M&S of CAs for agent-defeat, reaction mechanisms and kinetics, while important, are not the only aspects to consider when choosing a simulant for study. The researchers provided insight into the properties of importance for various scenarios such as container failure, droplet formation and breakup, evaporation, neutralization, and pool fires. Each situation is sensitive to different parameters so one must be careful in assessing the process being studied. For container failure, the researchers are under the opinion that for all modes of liquid release and primary droplet formation, the critical parameters for a simulant to match are the liquid density, equation of state, and surface tension. For droplet breakup, surface tension is likely the most important factor to consider. For evaporation, the latent heat of vaporization and vapor pressure across the temperature range of interest are most important. For neutralization, Arrhenius coefficients for the rate determining step and products of that reaction (i.e., reaction pathways) are crucial properties as well as the heat of combustion. It may also be necessary to choose a simulant with very similar primary and secondary reactions as the CA. Pool fire assessments are underway to determine what the critical properties to mimic are.

2.5 Current Testing Capability Development, Dr. James Lightstone, NSWC-IHEODTD

This presentation gave an overview of the dedicated facilities developed recently for chemical agent defeat testing at NSWC-IHEODTD. The briefing showed the progress of installation of the detonation and exhaust chambers built specifically for agent/simulant testing (similar to the setup used by DSTL) in contrast to the chambers used for current biocidal agent testing. NSWC-IHEODTD's

test chambers include thermocouple and pressure gauges for temperature and pressure monitoring, as well as other diagnostic capabilities.

2.6 Basic Research Efforts

The next four presentations will summarize research goals and objectives each of the investigators has proposed to the Period E BAA.

2.6.1 Chemical Reactions and Kinetics of CWA Simulants under Extreme Heating Conditions, Dr. Hergen Eilers, Washington State University (WSU)

The proposed project's goals and objectives include developing a means for monitoring chemical reactions during very fast heating of CWA simulants and identifying decomposition products and kinetics of rapidly heated simulants in the presence of different background gases, with or without reactive compounds, and with potentially neutralizing surfaces. The approaches shown were droplet generation and heating using an ultrasonic high temperature atomizer and generator and a pyroprobe heater for achieving heating rates up to 20,000 degrees/s. Optical and non-optical in- and ex-situ characterization techniques to be used for identification of reaction products and kinetics include: optical emission spectroscopy, laser-based UV absorption spectroscopy, UV/VIS spectroscopy, FTIR with kinetics mode, Raman spectroscopy, GCMS, time-of-flight mass spectroscopy, and other techniques.

2.6.2 High Temperature Decomposition Pathways and Intermediate Concentrations of Simulants Using Shock Tube and Time-Resolved Laser Absorption Diagnostics, Dr. Subith Vasu, University of Central Florida (UCF)

This presentation began with the PI reiterating that knowledge about intermediate species and their formation time-scales are absent at high heating rates and fast time scales—information that is needed for model validation. A summary of high temperature simulant data from literature was then given including setup/simulation information from various references. For DMMP, experiments with a nozzle burner with propane/air premixed flame at 1 atm were done as explained in Jayaweera et al. (2004), "Flame Suppression by Aerosols Derived from Aqueous Solutions Containing Phosphorus", *Combustion and Flame*, 141, pp. 308-321. Vasu's presentation also outlined the DIMP simulations from Glaude et al. (2002) and Zegers and Fisher (1998) as well as the TEP studies in the latter. For DEMP, he mentioned turbulent flow reactor studies at 1 atm and 802-907 K from Zegers et al. (1996), "Gas-phase Pyrolysis of Diethyl Methylphosphonate", *Combustion Science and Technology*, 116(1-6), pp. 69-89, and PM3 semi-empirical estimations made in Glaude et al. (2000).

Vasu gave an overview of his proposed work which includes high purity shock tube experiments within a wide range of temperatures and pressures (800 to 2200 K and 1 to 10 atm, respectively) conducted using mid-IR absorption spectroscopy and the methodologies involved in modeling high temperature chemical kinetics. Shock tube experiments are advantageous in that they act as a near-ideal constant volume reactor, with well-determined

initial temperature and pressure and can provide optical access for larger diagnostics. His experimental efforts involve pyrolysis and combustion experiments in the shock tube with varying oxygen concentrations and a look at species time histories. Diagnostics will be used to measure rates of key reactions. Chemical kinetic model validation and refinement will also be done. Reaction mechanism development will explore decomposition pathways, intermediate species sub-mechanisms, full and reduced mechanisms, and validation.

One interesting find shown in this presentation involving mid-IR spectra for laser diagnostics development was a plot of decadic absorbance spectra as a function of wavelength for CAs and simulants taken from Qu et al. (2012), "Detection of chemical warfare agents based on quantum cascade laser cavity ring-down spectroscopy", in *Chinese Optics Letters*, 10:5, pp. 050102. The plot showed that IR spectra peaks were most prominent in the 9-11.5 μm region for many of the agents and simulants. As such, laser wavelength selection in the PI's experiments will be made after high-resolution FTIR measurements confirm promising wavelengths.

2.6.3 Measurement of Decomposition and Inactivation Mechanisms of CWA Simulants at High Heating Rates, Dr. Travis Sippel, Iowa State University (ISU)

This talk summarized the proposed efforts of heating simulants and simulants with biocides at heating rates spanning from deflagration (10^4 °C/s) to near-detonation (10^7 °C/s) thermal regimes. This work aims to investigate thermal decomposition of simulants and inactivation in the presence of gas- and condensed-phase biocides. The approach of the proposed work is broken down into three steps: integrating controlled, high heating rate experiments with high speed optical diagnostics, implementing the use of two primary heating techniques (electrically heated filament for rates between 10^4-10^7 °C/s and IR laser irradiation) for investigation of both gas-phase and condensed-phase CWA simulants and biocides, and using a broad range of high repetition rate techniques for investigation of IR absorption.

Electric filament heating (T-jump experiments) uses capacitive discharge filament heating with controlled gas environment and can be provide near wire surface heating of liquid or vapor simulants. Sub-microsecond (~10s of ns) temporal speciation will be achieved using monochromatic IR absorption, ns vibro-Raman Spectroscopy, and fs/ps point Coherent anti-Stokes Raman Spectroscopy (CARS). Filtered Rayleigh scattering and 2-color video pyrometry will be used for gas-phase and condensed-phase temperature measurements, respectively, along with fs/ps N_2 CARS. For phase detections, time resolved (phase-locked) UV/VIS vapor fluorescence will be used as outlined in Michael et al. (2010), "Subcritical Microwave Coupling to Femtosecond and Picosecond Laser Ionization for Localized, Multipoint Ignition of Methane/Air Mixtures", *J. Appl. Phys.*, 108, pp. 093308-10.

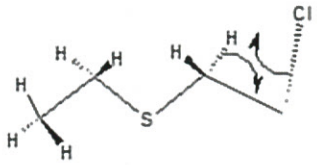
The PI described an initial low heating rate screening of CWA decomposition/inactivation mechanisms using DSC/TGA and MS/FTIR between ~1-100 °C/min. As described in Feng et al. (2014), "Thermal Ignition Dynamics of Aluminum/Polytetrafluorethylene Nanocomposite

Particles: Influence of Gas Environment", in *AIChE Annual Meeting,* (Atlanta, GA), speciation of compositions at slow heating rates at low repetition rates will be used to initially select targeted wavelengths of interest in ns-IR absorption with MS providing trace species detection and high selectivity. Low-speed broadband experiments provide insight into specific species to target at ultrafast repetition rates and higher heating rates. For speciation, targeted wavelengths will be selected based on lower speed FTIR detection experiments, i.e., FTIR step scan and DSC/TGA-FTIR. The fs/ps N_2 CARS spatio-temporal species and temperature mapping will combine broadband pump source with two narrow sources and can enable simultaneous multi-species quantization, a robust technique widely used in highly multiphase environments, as described in Dedic et al. (2015), "Hybrid fs/ps coherent anti-Stokes Raman scattering in a non-equilibrium environment initiated by a ns laser spark", *46th AIAA Plasmadynamics and Lasers Conference,* AIAA Aviation, (AIAA 2015-2962), Dallas, TX.

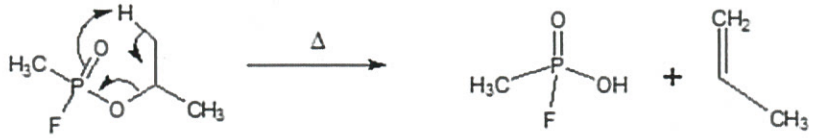
2.6.4 Designing Safe, High Fidelity Simulants, Dr. Matthew Blais, Southwest Research Institute (SwRI)

The most important point made in this presentation was that we must decide what critical property of the actual agent should be matched in the simulant. We know that we cannot find a simulant that mimic all the properties of a CA, such as vapor pressure, boiling point, viscosity, density, linear diffusion, solubility, oxidation potential, combustion properties, etc. For these high-temperature chemistry investigations, Blais suggested that the most critical property is the activation barrier to reaction. In addition, he explained that physical properties taken from literature sources, especially older sources, could be dependent on the method of measurement and diagnostics. For example, SwRI has measured the activation energy (E_a) for HD to be 48 kcal/mol, while the published value is between 22-36 kcal/mol.

Blais summarized works done at SwRI involving thermal defeat of CAs, including understanding the type of decomposition reaction and what the activation energies are. For HD, the decomposition mechanism is not definite, and is speculated by *ab initio* modeling of the CEES (half mustard molecule) to follow this, with a measured activation barrier of 48 kcal/mol:



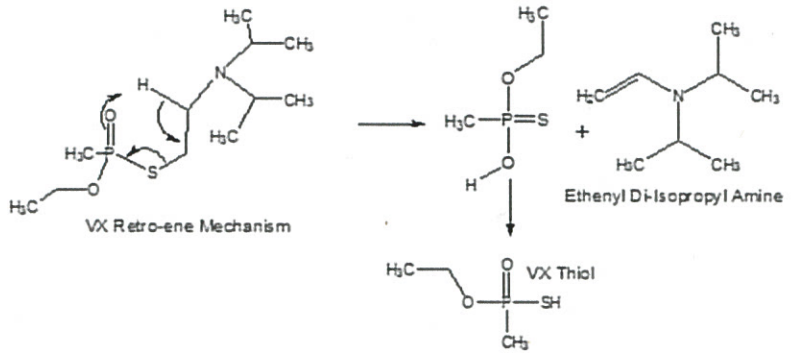
GB undergoes a retro-ene type of decomposition reaction between 300 and 1000 K.



Mechanisms above this temperature range are likely hemolytic cleavage-generating radicals. SwRI measures the activation energy for this reaction to be 36 kcal/mol. The literature value is 40 kcal/mol so there is good agreement there.

VX decomposition was observed to occur via the production of an ethenyl di-isopropyl amine,

with a measured E_a of 39 kcal/mol.



Research plans for the future were also presented which include testing of agents in reactive atmospheres (O_2, humidity, acid gases, and oxidizing environments) and investigating pool fires to determine if agents can sustain pool fires in air and in oxygen depleted conditions.

3. Discussion

The two-hour discussion centered on the important physical parameters/criteria to be considered for choosing a set of simulants for these high-T studies, and then using those criteria for choosing a set of simulants to be studied. The criteria deemed important were the molecular structure, activation barrier to high-temperature reaction, the evaporation rate, and of course the safety/toxicity. Further reactions with interfaces like crucibles, glass, etc. were also considered. When possible, if a high-T reaction mechanism could be speculated, the group then discussed the evaporation and safety of the by-products of high-T reactions of the simulants being discussed. This was important, for example in the burning of TEP to produce ethylene as a byproduct, which contributes to burning, and changes the burning rate being measured for TEP.

Keeping all that in mind, the discussion continued to seek simulants for each of the three known agent 'classes' HD, GB, and VX. The simulants considered for each were taken from Bartelt-Hunt et al. (2008):

- Mustard (HD) and simulants - CEES (Half-Mustard), CEPS, Diethyl malonate, CEMS, Diethyl adipate, Methyl salicylate, Diethyl pimelate, and Dimethyl adipate
- Sarin (GB) and simulants – BUSH, TMP, DEEP, Paraoxon, DMMP, DPCP, DFP, TEP, DEM, DIMP
- Nerve Agent VX and simulants – DEP, DES, BIS, Malathion, DEM, Parathion, DEPPT, and Amiton.

Other simulants were also presented by the group, or brought up during the discussion. More information on these simulants can be found in Appendix B.

3.1 HD (sulfur mustard)

For HD, 2-chloroethyl-ethyl sulfide (CEES), also known as half-mustard (HM), was identified as a simulant of interest. SwRI has done liquid and vapor activation energy studies on this simulant, and therefore could do further investigations of reactions mechanisms, kinetics, etc. These older studies, however, were performed using an older test setup, and their future studies would need to be retested in their new experimental set up. SwRI added that CEES has about 10% of the vesicant

properties of HD and likely a carcinogen. More information on CEES can be found in Appendix B.

2-CEPS was rejected as a simulant for HD, after SwRI provided information that 2-CEPS is $1/7^{th}$ (~15%) as powerful as HD as a vesicant, very hazardous, and likely a carcinogen and mutagen. ECBC provided information that CECPRS (2-chloroethyl-3-chloropropyl sulfide), an HD impurity, may be more toxic than some studies can tolerate, but that it's physical properties are known. This may be possible simulants to study for HD. ECBC also relayed that CEIAS (chloroethyl iso-amyl sulfide), another simulant, has excellent vapor pressure, but may not be commercially available. This would limit testing of CEIAS. Both CECPRS and CEIAS may be considered pending further information received.

Methyl salicylate (MeS), another surrogate of interest discussed, has been confirmed to be a poor simulant for HD. From a chemical standpoint, beyond its solubility being off, in the present context of reaction kinetics, the frequency factor (A) and activation energy are also dissimilar to that of mustard. Also, it does not contain a sulfur atom. Hydrolysis and other neutralization work will be affected by this large chemical and structural difference. Without a chloride atom on the second carbon to function as a leaving group, the high reactive HD 3-membered sulfonium ring cannot form and thereby, react. In addition, it has been determined that the auto-ignition temperature of MeS is too high for HD simulation. Therefore, MeS is unsuitable as a simulant for HD with respect to flammability and chemical structure/reactivity reasons.

3.2 GB (sarin)

Three simulants were identified for GB are TEP (triethyl phosphate), DIMP (di-isopropyl methylphosphonate), and DEMP (diethyl methyl phosphonate) because of their evaporation rates and group's opinion on activation barriers to first reaction step, etc. DMMP was also considered. TMP (trimethyl phosphate) and DMHP were rejected as a possible simulant for GB because it does not undergo the same "retro-ene" decomposition mechanism as GB.

3.3 VX (O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate)

Three simulants were identified: TBP (tributyl phosphate), DEP (diethyl phthalate), and TEHP (tris(2-ethyl 1-hexyl) phosphate). It was noted that TBP was already being used in some medium-scale DoD tests, and TEHP had been used in testing by the Navy and by UK's DSTL. However, TEHP may have a higher activation barrier than VX, and further information was necessary for determination.

4. Summary

Very limited data exists in the conditions of interest (high temperatures, high heating rates) for simulating weapon defeat of targets containing chemical agent. DTRA is attempting to address this gap by funding basic research in this area. The purpose of the workshop was to identify and decide on a set of chemical simulants that would be most suitable for studying the reactivity and kinetics of chemical agents under extreme temperature and heating rate conditions within a post-blast fireball. The expectations were

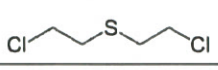
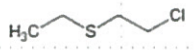
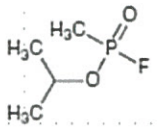
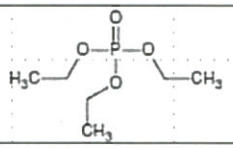
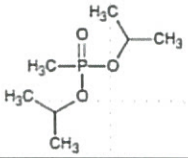
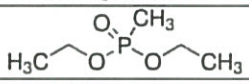
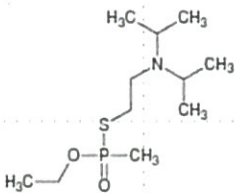
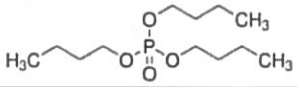
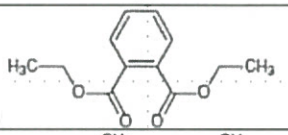
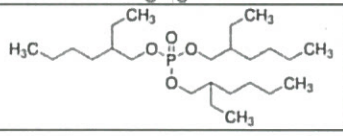
to identify three to five simulants per chemical agent of interest, so as to focus future basic research investigations. Appendix B summarizes chosen simulants and possible future basic research investigators that may study these.

While we have made an effort to find the best simulants for each agent of interest, it is important that the community remember that simulants and agents will have different chemical reaction, reaction kinetics and physical properties, and never completely simulate the actual chemical agent. Also highlighted throughout the workshop was the fact that the reaction kinetics and mechanisms obtained from these research projects may not be exactly the same at different pressures, temperatures and heating profiles. However, this research on the topic "Chemistry of Chemical Agents, Simulants, and Precursors" to be executed starting FY16 is an excellent beginning to solve the very difficult challenge of simulating the full effect of counter-WMD operations on targets containing chemical agents.

Appendix A: Workshop Agenda

WORKSHOP AGENDA		
8:00-8:30 am	Registration and Check-in	
8:30-9:00 am	Welcome, Introductions, Workshop Scope	Allen Dalton (DTRA)
9:00-9:20 am	Status of Chemical Agents and Simulants from Literature	Yasmine Aly (DTRA)
9:20-10:00 am	Physical Properties of Chemical Simulants	David Tevault (ECBC)
9:40-10:00 am	Selection of Chemical Agent Simulants	DSTL
10:00-10:20 am	A Modeler's Perspective	Andrea Zambon (CRAFT-Tech)
10:20-10:45 am	Break	
10:45-11:15 am	Current Testing Capability Development	James Lightstone (NSWC-IH)
11:15 am-12:15 pm	Basic Research Efforts	Hergen Eilers (WSU) Subith Vasu (UCF) Travis Sippel (ISU) Matthew Blais (SwRI)
12:15-1:30 pm	Lunch	
1:30-3:30 pm	Discussion	Su Peiris (AFRL)
3:30-4:00 pm	Review Action Items and Close	Allen Dalton

Appendix B: Selected Simulants and Potential Researchers who could Investigate High-T Reactions of these Simulants.

Agent	Simulant	Name	CAS	Structure	Potential Researchers
HD 	HM/CEES	half-mustard; 2-chloroethyl-ethyl sulfide	693-07-2		SwRI
GB 	TEP	triethyl phosphate	78-40-0		WSU
	DIMP	di-isopropyl methylphosphonate	1445-75-6		UCF, ISU, WSU
	DEMP	diethyl methyl phosphonate	683-08-9		UCF, WSU
VX 	TBP	tributyl phosphate	126-73-8		WSU
	DEP	diethyl phthalate	84-66-2		WSU
	TEHP	tris(2-ethylhexyl) phosphate	78-42-2		WSU

Appendix C: Comparison of Some Physical Properties of Agents and Simulants

Agent and Simulant	E_a, kcal/mol	A	Vapor Pressure, mm Hg, (25 °C)	Heat of Vaporization, cal/g	Viscosity, cp	Boiling Pt at STP, °C	Liq. Density, g/cc
HD	48	7.16×10^{12}	0.11	94	3.95	217	1.27
HM/CEES				85.1		157	1.07
GB	36.3	8×10^{11}	2.9	80	1.28	158	1.09
TEP	41.3	2.4×10^{15}	0.11	57.0	1.46	209	1.07
DIMP	41.2	2.3×10^{13}	0.339	76.4		215	0.976
DEMP	45.3	1.0×10^{13}	0.420	87.8		194	1.041
VX	39	2.7×10^{11}	0.0007	78.2	9.96	298	1.0083
TBP						289	0.9727
DEP						295	1.12
TEHP						450	0.92

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